

(19)



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Office européen des brevets



(11)

EP 0 749 128 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
18.12.1996 Bulletin 1996/51

(51) Int Cl.⁶ H01B 3/18, H01B 3/44

(21) Application number: 96304042.3

(22) Date of filing: 04.06.1996

(84) Designated Contracting States:
DE FR GB

(30) Priority: 12.06.1995 US 489423

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(54) **Filling compound for use in cables and spliced cable connectors**

(57) An improved filling material having superior properties in inhibiting fungal growth and wire corrosion is disclosed. The material is a styrene block copolymer

dissolved in naphthenic or paraffinic oil, containing polyethylene and containing a fungus and corrosion inhibitor such as 2-(4-thiazolyl)-benzimidazole.



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Description

TECHNICAL FIELD

5 This invention relates to a filling compound for use in cables and connectors used for connecting corresponding electrical conductors of two cables at a splice location. More particularly, the invention relates to a filling compound which waterproofs, insulates and reduces contamination in cables and connectors caused by dirt, dust, fungus, water and other contaminants.

BACKGROUND OF THE INVENTION

10 Cable used in the telecommunications industry, such as in telephone systems, generally requires a waterproofing filling material in the cable to protect the cable from water entry. This is true whether the cable is buried beneath the ground or laid under water. Waterproofing is also sometimes required in aerial applications. Attempts to waterproof cable, such as buried cable, began nearly 100 years ago and were unsuccessful in a practical sense until the introduction of plastic insulated cable during the 1950's. Since 1970, large quantities of cable have been filled with waterproofing compounds. This approach followed the recognition that in plastic insulated cable the localized intrusion of water into the cable sheath is not in itself a serious problem. Disruption or deterioration of service occurs when long lengths of cable become flooded. Flooding occurs because water that penetrates into a localized opening in the cable sheath is free to channel as far as gravity allows, often hundreds of feet. A solution that has been widely adopted is to fill the voids within the cable with a water insoluble filling material that simply plugs the cable to channeling water. Such filling material is disclosed in U.S. Patents 4,176,240 of Sabia and 4,259,540 of Sabia, which disclosures are incorporated by reference herein.

25 The Sabia filling material is a styrene-ethylene butylene-styrene triblock copolymer (SEBS) dissolved in mineral oil, with polyethylene added for consistency. The material was carefully tested for use in underground cables and thus the major considerations in evaluating the composition were its viscosity, temperature stability and mechanical characteristics such as handleability. An acceptable composition for this application ranges from about 5 - 7% SEBS, 87 - 91% mineral oil, and 2 - 6 % polyethylene. The composition disclosed contains no protective ingredients and thus if water or another contaminant penetrates the physical boundary created by the filling compound it will cause contamination of the filling compound and corrosion of the cable. If used above ground, this filling material would be more susceptible to fungal and other types of contamination and would tend to become contaminated. In addition, the filling compound taught has a tendency to flow out of above ground cables, especially where solar heating (up to 80°C) is a factor.

35 United States Patent 4,870,117 of Levy, which disclosure is incorporated herein by reference, represents an attempt to solve the problem of heat sensitivity of the filling compound disclosed in U.S. Patents 4,259,540 and 4,176,240. The filling compound disclosed is for use with aerial cables and employs a styrene rubber (styrene-ethylene butylene) (SEB) diblock copolymer to replace all or part of the SEBS used for filling underground cables. SEB has a lower physical crosslink density which results in the oil of the composition being more effectively gelled. Accordingly, separation and flow of the filling compound at elevated temperatures is significantly reduced or eliminated. However, this composition also does not possess any anti-fungal or anti-corrosive properties.

40 In the communications industry it is commonplace for two cables to be connected at one or more splice locations. Typically, each cable comprises a multitude of individual conductors which must be spliced to join the cables. It has been estimated that over two billion pair splice connections are made each year by the telephone industry. It is obviously important in the industry for these splice connections to be durable and, preferably, permanent connections.

45 Typically, the individual conductor ends to be spliced are brought and held together in multiple contact connectors such as the one disclosed in United States Patent 3,858,158 of Henn et al., which disclosure is incorporated herein, by reference. To protect the conductors, the connector is commonly packed with a filling compound which is meant to prevent the conductors from contacting water and other contaminants, inasmuch as the exposure of spliced conductors to water and other contaminants lowers the life-time of the connections. Not only is the capacitance balance of transmission lines upset but also serious corrosion may occur. Telephone companies spend many hours and much expense repairing lines and restoring telephone service following such damage to conductors. A major problem is that once water or any other contaminant enters a cable or a multiple contact connector, it typically spreads through the filling compound to all of the conductors within the connector and, as a result, the entire connector must be replaced and each conductor re-spliced. Therefore, to prevent the above problems, these companies, for example, have developed filling compounds for use in connectors. Although the physical function of the connector filling material is straightforward, the choice of the material is not. Among the many parameters or characteristics that have in the past been considered important for materials used in this application are the hydrophobic nature of the material, its stability on aging, low temperature properties, flow characteristics at elevated temperatures, processing characteristics, handling character-

istics, dielectric properties, toxicity, and cost.

The filling compounds for use with cables as described above are not suitable for use in connectors. A lower viscosity material is used for connectors so that the filling compound will disperse within the voids created by the electrical conductors and the structure of the connector. This problem has been solved in the industry by using a material having a higher amount of oil and/or different amounts of SEBS and polyethylene. However, such a filling compound suffers from the same problems as the above filling compounds for use in cables in that contamination of the filling compound may occur, which results in corrosion of the electrical conductors.

Filling compounds of the types as above described have been used in the industry and have been the source of user complaints due to yellowing of the filling compound. This yellowing further has been seen to lead to corrosion and loss of telephone service. Therefore, if this filling compound is used in connectors, the filling compound and the spliced conductors still are susceptible to corrosion and contamination over time due to contact with various contaminants such as fungus, dirt, water, etc. and telephone service may be interrupted.

As is apparent from the foregoing discussion, it is a problem in the industry that the filling compound in cables and spliced cable connectors is contaminated by exposure to water, dirt, dust, fungus, insects and other contaminants. This contamination eventually will cause decay of the filling compound and corrosion of the conductors. Loss of telephone service will result along with the need for expensive repair by the telephone company.

SUMMARY OF THE INVENTION

The foregoing problems are overcome by a filling compound in accordance with the present invention, which includes an ingredient which imparts protective properties to the filling compound. More particularly, the inventors of the present invention have discovered that the above discussed yellowing and contamination problems can be eliminated by including an anti-fungal ingredient in the filling compound. Surprisingly, the inventors discovered that the anti-fungal ingredient additionally provides significant anti-corrosive protection for the electrical conductors when present in the compound in a particular range.

The invention is characterized in that the filling compound comprises a mixture of a styrene-ethylene butylene-styrene triblock copolymer (SEBS), oil such as mineral oil, a low molecular weight polyethylene, and an antifungal and anti-corrosive ingredient. Additionally, the filling compound may comprise a copper deactivator, a styrene-ethylene-butylene (SEB) diblock copolymer and/or polybutene oil. Specifically, an anti-fungal compound which has been demonstrated to be effective in connectors is 2-(4-thiazolyl)-benzimidazole. The filling compounds of the invention have suitable temperature flow, capacitance stability, and processing characteristics equivalent to those of prior art materials and, further, significant anti-corrosive properties. In addition, a cable or connector filled with the filling compounds of the invention experiences essentially no growth of fungus.

DETAILED DESCRIPTION

The filling compound of the present invention is an improvement over the filling compounds disclosed in U.S. Patents 4,176,240, 4,259,540 and 4,870,117 in that it retains all of the positive attributes of the filling compounds disclosed therein and, in addition, has resistance to contamination and protects the conductors from becoming corroded due to exposure to fungus, dirt, and other contaminants. The inventors have found that the addition of an anti-fungal ingredient substantially improves the ability of the filling compound to resist corrosion and contamination. A preferred embodiment of the invention incorporates 2-(4-thiazolyl)-benzimidazole which is known in the art to be a preservative which effectively controls mold and mildew on paint films and on natural and synthetic fibers but has not, insofar as applicants are aware, heretofore been used in a cable filling compound. The preservative is sold specifically for use in protecting natural and synthetic carpet fibers, surface coating films and canvas textiles by Calgon Corporation under the trade name "TK-100". In addition to these known properties of the chemical, the inventors have found that, surprisingly, the chemical also imparts significant anti-corrosive properties to the filling compound when present in the amount specified herein, properties which are not anticipated in the prior art. One formulation of the filling compound of the invention is set forth in Table 1. This formulation was arrived at to impart the desired physical and chemical properties to the filling compound used in connectors.

TABLE 1

Constituent	Description	Parts By Weight
styrene-ethylene butylene-styrene triblock copolymer (SEBS)	Viscosity at 23°C at 20 wt % in toluene from about 1300 - 1700 centipoises by ASTM D 445. Available from Shell Chemical Co. under the trade designation Kraton G 1650. Styrene to rubber ratio from about 0.2 to 0.5.	3.0 ± 0.15
Oil	Extender Oil type 104B per ASTM D 2226. Available from Penreco as Drakeol 35. Also available from Amoco as White Mineral Oil # 31 or # 35.	91 ± 1
Low Molecular Weight Polyethylene	Drop melting point is 91°C according to ASTM D 127. Available from Allied Chemical Corporation under the trade designation AC9CF.	6 ± 0.25
Antioxidant	Available from Ciba Geigy under the trade designation Irganox 1035.	0.5 min.
Copper Deactivator	Available from Ciba Geigy under the trade designation Irganox 1024.	0.05 ± 0.005
Dye	Available from Keystone Aniline Chemical Company as Oil Blue A.	0.002 min.
Fungal and Corrosion Inhibitor	Available from Calgon Corporation under the trade name Metasol TK-100.	0.01-0.25

The formulation is prepared as described hereinafter. Preheat the oil with the Irganox 1035 and Irganox 1024 to 130 ± 5°C and add the other components while stirring. Stir until a homogeneous mixture free of agglomerates is obtained. Increase the blend mixture to 150°C for a minimum of 1 hour and a maximum of 2 hours. Maintain an inert gas blanket such as N₂ or CO₂ over the mixing vessel during the 150°C portion of the mixing cycle.

The amount of fungal and corrosion inhibitor is variable as long as the characteristics of the final compound are acceptable. Amounts from about 0.01 to 0.25 parts by weight are sufficient to impart desired qualities to the filling compounds of the invention. While this range is the preferable range it is apparent that amounts above 0.25 parts by weight may be used if the other properties of the filling compound are not negatively affected. However, amounts greater than 0.25 parts by weight of the compound 2-(4-thiazolyl)-benzimidazole would generally be considered economically unfeasible.

The composition prepared as in Table 1 should have the properties as in Table 2.

TABLE 2

PROPERTY	VALUE
Viscosity cP at 110°C	39 ± 3 per ASTM D 2639
Drop Melting Point °C	89 per ASTM D 127
Slump at 75°C	Pass MS-17000, Section 1061 except modified as follows: Place 20 gms of material in each of four aluminum dishes (No. 8-730C from Fisher Scientific Co.). Heat to 130°C until melted. Condition for 16 to 24 hours at room temperature. Place dishes on a side (90° angle) in an oven at 75°C for a minimum of 2 hours.
Cone Penetration 0.1 mm at room temperature	160 - 190 ASTM D 217. Prepare suitable specimen by heating to 130°C until melted. Condition for 16 to 24 hours at room temperature.

TABLE 2 (continued)

PROPERTY	VALUE
Oxidative Stability at 200°C, minutes	10 per MS-17000, Section 1230 Procedure B using copper pans
Volume Resistivity, ohm-cm	10 ¹⁴ minimum per ASTM 257. Prepare specimen per MS-17000, Section 1057 and test per flat specimens using unequal electrodes. Top electrode shall be foil without guard electrode. bottom electrode shall be shallow brass dish to hold the specimen. Measure the resistivity after one minute at 100 - 550 volts DC.

The composition of Table I has been evaluated in terms of anti-fungal activity as well as anti-corrosive activity. The anti-fungal test was done in accordance with the specifications of the ASTM G-21 and FOTP-56 tests for fungal growth. The samples, numbered as follows were 1) a specimen of the filling compound prepared as in the foregoing; 2) a specimen of the filling compound prepared as in the foregoing without the fungal and corrosion inhibitor; and 3) a strip of cotton duck. Each sample was placed in a petriplate and the petriplates were then inoculated with a mixed spore suspension by means of a fine mist atomizer. The following fungi were used:

Fungus	ATCC Number	
Aspergillus niger	6205	9642
Penicillium funiculosum		11797
Chaetomium globosum		9645
Gliocladium virens		15233
Aureobasidium pullulans	11730	9643
Aspergillus flavus		
Aspergillus versicolor		

The inoculated specimens were incubated at +28°C to +30°C at not less than 85% relative humidity for a period of twenty-one days. Fungal growth was recorded at the end of each week in accordance with paragraph 9.3 of ASTM G-21 as follows:

TABLE 3

OBSERVED GROWTH ON SPECIMENS	RATING
None	0
Traces of growth (less than 10%)	1
Light Growth (10 to 30%)	2
Medium Growth (30 to 60%)	3
Heavy Growth (60% to complete coverage)	4

The test results were as follows:

TABLE 4

Sample	Inspection at 7 Days	Inspection at 14 Days	Inspection at 21 Days
1	0	0	0
2	0	0	1
3	4	4	4

Copper strips coated with the filling compound were evaluated using the ASTM D 130 copper strip corrosion test. A small amount of sulfur was added to the compound to accelerate corrosion, since sulfur is a known corrosive agent. The results are summarized in Table 5.

TABLE 5

Temperature (°C)	Time (Days)	Standard Sealant + 50 ppm Sulfur	Standard Sealant + 50 ppm Sulfur + 0.05% TK-100
60	30	Corrosion	No Corrosion
90	1	Corrosion	No Corrosion

Thus, it can be seen from the above that the filling compound of the present invention substantially prevents contamination of the filling compound by fungus and prevents corrosion of copper wire. The filling compound prepared as in Table 1 is designed to be used in plural conductor connectors such as that disclosed in U.S. Patent 3 772 635 of Frey et al., which patent is incorporated herein by reference. It is anticipated that the invention in other embodiments is also suitable for use as a filling compound for cables, whether underground or aerial, and for other applications. For use in cables, the anti-fungal/anti-oxidant ingredient can be used in an amount ranging from about 0.025 to 0.25 parts by weight in compositions such as those disclosed in U.S. Patents 4 176 240, 4 259 540 and 4 870 117.

It should be understood that the above described arrangements are simply illustrative of the invention. Other arrangements may be devised by those skilled in the art which embody the principles of the invention and fall within the spirit and scope thereof.

Claims

1. A filling compound for use in a cable or spliced cable connector, comprising a mixture of
 - a styrene block copolymer;
 - polyethylene;
 - naphthenic or paraffinic oil; and
 - a fungus and corrosion inhibitor.
2. The filling compound of claim 1, wherein the copolymer is a styrene-rubber triblock copolymer having a styrene to rubber ratio of from about 0.2 to 0.5 present in an amount from about 3 to 7 parts by weight.
3. The filling compound of claim 1, wherein the polyethylene has a softening point of from about 110°C to 130°C and is present in amounts from about 2 to 6 parts by weight.
4. The filling compound of claim 1, wherein the fungus and corrosion inhibitor is 2-(4-thiazolyl)-benzimidazole present in amounts from about 0.01 to 0.25 parts by weight.
5. The filling compound of claim 1, wherein the oil is type 104B oil per ASTM D 2226 present in amounts from about 87 to 91 parts by weight.
6. A filling compound for use in a cable or spliced cable connector, comprising
 - from about 0.9% to 5% styrene-rubber triblock copolymer having a styrene to rubber ratio of from about 0.2 to 0.5;
 - from about 0.5 to 4.1 parts by weight of a 30/70 mixture of styrene-rubber triblock copolymer/styrene-rubber diblock copolymer;
 - from about 6.9 to 7.1 parts by weight of polyethylene;
 - from about 77 to 80 parts by weight naphthenic or paraffinic oil;
 - from about 7 to 10.2 parts by weight polybutene; and
 - a fungus and corrosion inhibitor.
7. The filling compound of claim 6, wherein the fungus and corrosion inhibitor is 2-(4-thiazolyl)-benzimidazole present in amounts from about 0.01 to 0.25 parts by weight.
8. A multiple contact connector for connecting spliced conductors, comprising
 - a casing for holding a plurality of spliced conductors and having voids within said casing and between the

spliced conductors; and

a filling compound for filling said voids comprising about 3 parts by weight styrene-ethylene butylene-styrene triblock copolymer having a styrene-rubber ratio of about 0.2 to 0.5, about 91 parts by weight type 104B oil per ASTM D 2226, about 6 parts by weight polyethylene having a drop melting point of at least 91°C per ASTM D 127 and 2-(4-thiazolyl)-benzimidazole present in amounts from about 0.01 to 0.25 parts by weight.

9. A filling compound for use in a spliced cable connector comprising

- approximately 3 parts by weight styrene-ethylene butylene-styrene triblock copolymer having a styrene-rubber ratio of approximately 0.2-0.5,
 - approximately 91 parts by weight type 104B oil per ASTM D 2226,
 - approximately 6 parts by weight polyethylene having a drop melting point of at least 91°C per ASTM D 127, and
 - from about 0.01 to 0.25 parts by weight fungus and corrosion inhibitor;
- wherein said filling compound has a viscosity of between about 36 and 42 cP per ASTM D 2669 and a drop melting point of about 89°C per ASTM D 127.

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